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Corrosion Resistance of Highly Alloyed Materials in 3.5% NaCl Solution at Elevated Temperature

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In this research electrochemical studies were performed on stainless steels and compared to Cunifer, Monel and Alloy 59 in 3.5% NaCl solution at (22±2) °C and (50±2) °C at 200 rpm. Those materials have been evaluated using weight loss, Tafel polarization, cyclic polarization and scanning electron microscopy techniques. Material with the best performance was Alloy 59 which could be used in the seawater environment at (22±2) °C and (50±2) °C. Materials with very high percentages of chromium and molybdenum showed high resistance toward selective corrosion and materials with high levels of copper showed excellent resistance toward pitting corrosion.

Keywords: Alloy; Weight loss; SEM; De-alloying; Pitting corrosion

1. INTRODUCTION

Many marine structures, at some stage of their life span, come into contact with the heated seawater. Corrosion, usually pitting, occurs on the walls of these structures and can quickly lead from surface damage and aesthetics impairment to deeper damage. The main causes of the corrosiveness are chloride ions which facilitate initiation and propagation of pits particularly at elevated temperatures. Stainless steels provide a wide range of applications in seawater environments. They are used for the construction of heat exchangers, tanks and capacitors for electrical systems, refrigeration systems for power plants, power plants driven by waves, tidal power, wind turbines localized at sea and desalination plants [1-4].

Stainless steel type 304 in the sea water is susceptible to pitting corrosion at 10 °C, and the more resistance steel type 316, could easily reach the same perforation with a small temperature increase [5-12].

Deng et al. [13] have demonstrated that the temperature range in which W.Nr. 1.4462 still has the repassivation capability is from 34.9 °C to 59.2 °C, and higher temperature is so-called critical pitting temperature at which the materials will be affected by pitting corrosion. For the material W.Nr. 1.4410 the repassivation capability is from 70.9 °C to 87.6 °C. Corrosion of structural materials is also caused by the sea atmosphere which is constantly saturated with salt. In addition, the wind causes the deposition of sea salt on all exposed surfaces, and with the oxygen and high average temperatures, all conditions for the formation of corrosive atmosphere are met [14-19].

The aim of this research was to determine corrosion resistance in seawater simulated environment at (22±2) and (50±2) °C of six different materials recommended as suitable materials for use in marine environment.

2. EXPERIMENTAL

Physical and chemical properties of the tested materials are given in the Table 1. The working area of test samples was 1 cm^2. All samples were gradually polished with the sandpapers with different grits with the final machining quality N6, so that the maximum deviation of the roughness profile was R_{max} = 2.5 μm. Afterwards, samples were degreased in ethanol and rinsed with demineralized water. DC electrochemical corrosion tests were conducted in accordance with ASTM G5-94 [15] on the device Potentiostat/Galvanostat Model 273A EG&E with the SoftCorr III application. Measurements were carried out in relation to the reference saturated calomel electrode (SCE) with known potential of +0.242 V versus standard hydrogen electrode (SHE). The parameters of general corrosion were determined: corrosion potential (E_{corr}), corrosion current density (j_{corr}), corrosion rate (v_{corr}), polarization resistance (R_p), pitting potential (E_{pit}) and protective pitting potential (E_{ppit}).

Table 1. Physical and chemical properties of materials

Sample	Common name	W.Nr.	Cr, %	Ni, %	Mo, %	Cu, %	E_w, g	ρ, g/cm^3
1.	Cunifer	2.0882	-	30	-	70	31	8.9
2.	S32205	1.4462	23	6	3	-	25.8	7.8
3.	S31050	1.4466	25	25	2.1	-	25.7	7.9
4.	Monel	2.4360	-	67	-	31	30.1	8.8
5.	Alloy 59	2.4605	23	59	16		27	8.6
6.	316L	1.4404	18	13	2	-	26.4	8

Where is:
***E**$_w$* – equivalent weight, *g*
ρ – density, *g/cm^3*

Electrochemical testing of all samples was carried out in 3.5 % NaCl solution, at 200 rpm a stirrer and at (22±2) °C and (50±2) °C. The temperature and steering speed were adjusted by Heidolph 3001 series magnetic stirring hotplate.

Weight loss measurements were performed according to the ASTM G48-G99 standard for examination and evaluation of pitting corrosion [16], in 10 % $FeCl_3$ solution for 72 hours. The samples were withdrawn, cleaned and weighted every 24 hours and returned in 10 % $FeCl_3$ solution.

After electrochemical measurements, the surface of the tested specimen was observed and recorded using stereomicroscope Leica MZ6 (low amplification). After weight loss measurements, topography of the samples was determined using scanning electron microscope VEGA TESCAN TS 5136 MM.

3. RESULTS

Tables 2 and 3 show DC test results at (22±2) °C and (50±2) °C of all samples. The highest corrosion current density was measured in samples W.Nr. 2.0882 at both temperatures. Samples W.Nr. 2.0882 (Cunifer) and W.Nr. 2.4360 (Monel) showed great tendency of selective corrosion (Figure 3). Other samples have shown good resistance to corrosion in chloride solution at (22±2) °C and (50±2) °C.

Table 2. DC test results at (22±2) °C

Sample W.Nr.	E_{corr} vs SCE [mV]	j_{corr} [nA/cm^2]	b_a [V/dec]	b_c [V/dec]	v_{corr} [mm/a]	R_p [kΩcm^2]	E_{pit} vs SCE [mV]	E_{ppit} vs SCE [mV]
2.0882	-194	11310	0.104	0.170	0.128	2.820	-50	-60
1.4462	-101	401	0.229	0.113	0.0043	64.31	320	110
1.4466	-132	256	0.240	0.094	0.0027	40.97	390	-10
2.4360	-204	1621	0.220	0.101	0.0181	13.43	-20	-150
2.4605	-220	552	0.234	0.241	0.0056	67.91	650	220
1.4404	-155	175	0.171	0.140	0.0019	73.25	290	-230

Table 3. DC test results at (50±2) °C

Sample W.Nr.	E_{corr} vs SCE [mV]	j_{corr} [nA/cm^2]	b_a [V/dec]	b_c [V/dec]	v_{corr} [mm/a]	R_p [kΩcm^2]	E_{pit} vs SCE [mV]	E_{ppit} vs SCE [mV]
2.0882	-207	26120	0.130	0.192	0.297	1.310	-60	-70
1.4462	-75	325	0.240	0.106	0.0035	47.71	250	-80
1.4466	-90	432	0.233	0.092	0.0046	31.63	280	-90
2.4360	-240	1664	0.224	0.068	0.0186	11.83	-40	-160
2.4605	-220	226	0.234	0.171	0.0023	131.3	550	-30
1.4404	-132	239	0.233	0.075	0.0025	35.23	250	-

Figures 1 and 2 show cyclic polarization diagrams at (22±2) °C and (50±2) °C. Sample W.Nr. 2.0882 does not show a tendency toward pitting or crevice corrosion. The sample is prone to selective corrosion due the standard electrode potential difference of nickel (-0.22 V) and copper (+0.33 V) versus standard hydrogen electrode (SHE). The elution of nickel after cyclic polarization, which is significantly more expressed at (50±2) °C, can be clearly visible on the Figure 3.

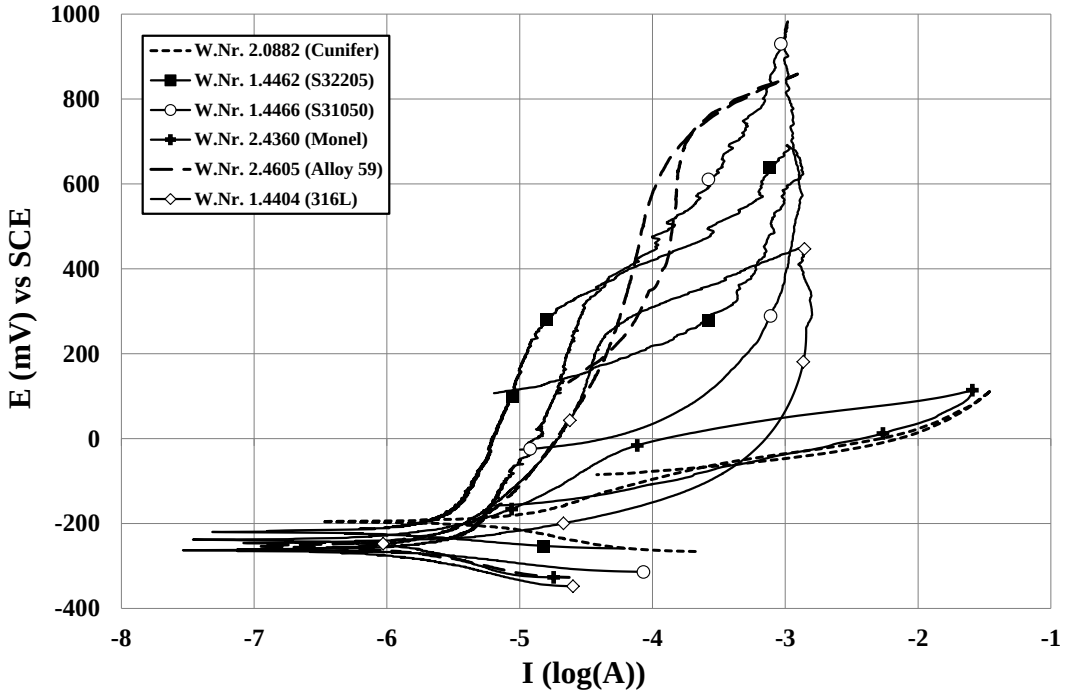
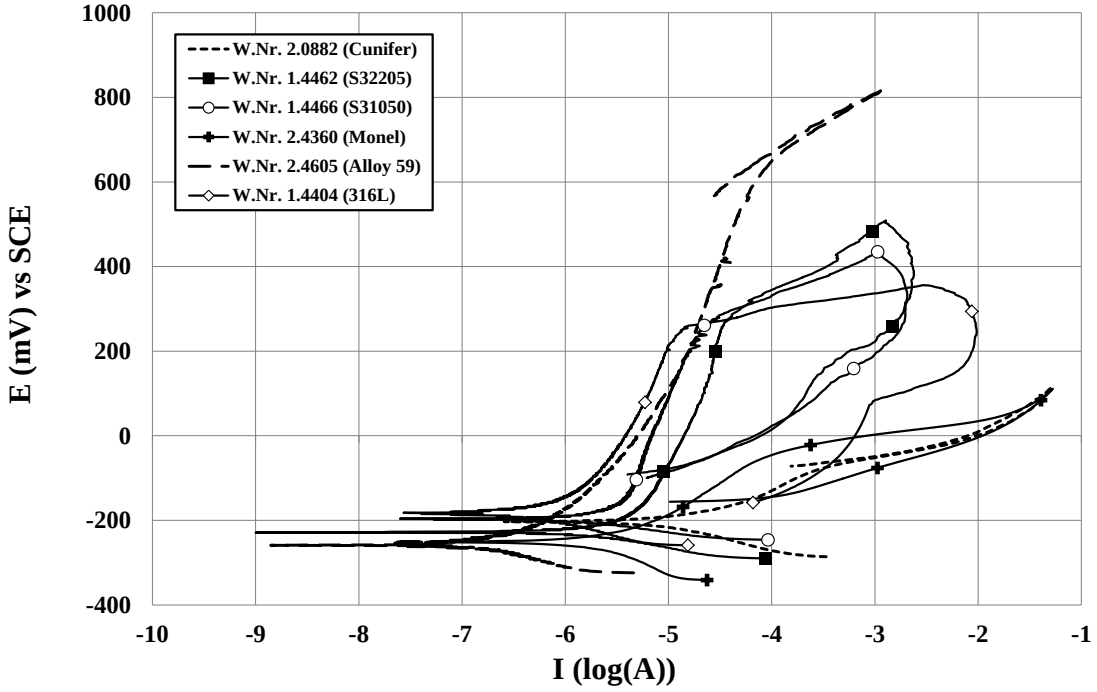


Figure 1. Cyclic polarization diagrams of all samples at (22±2)



°C

Figure 2. Cyclic polarization diagrams of all samples at (50±2) °C

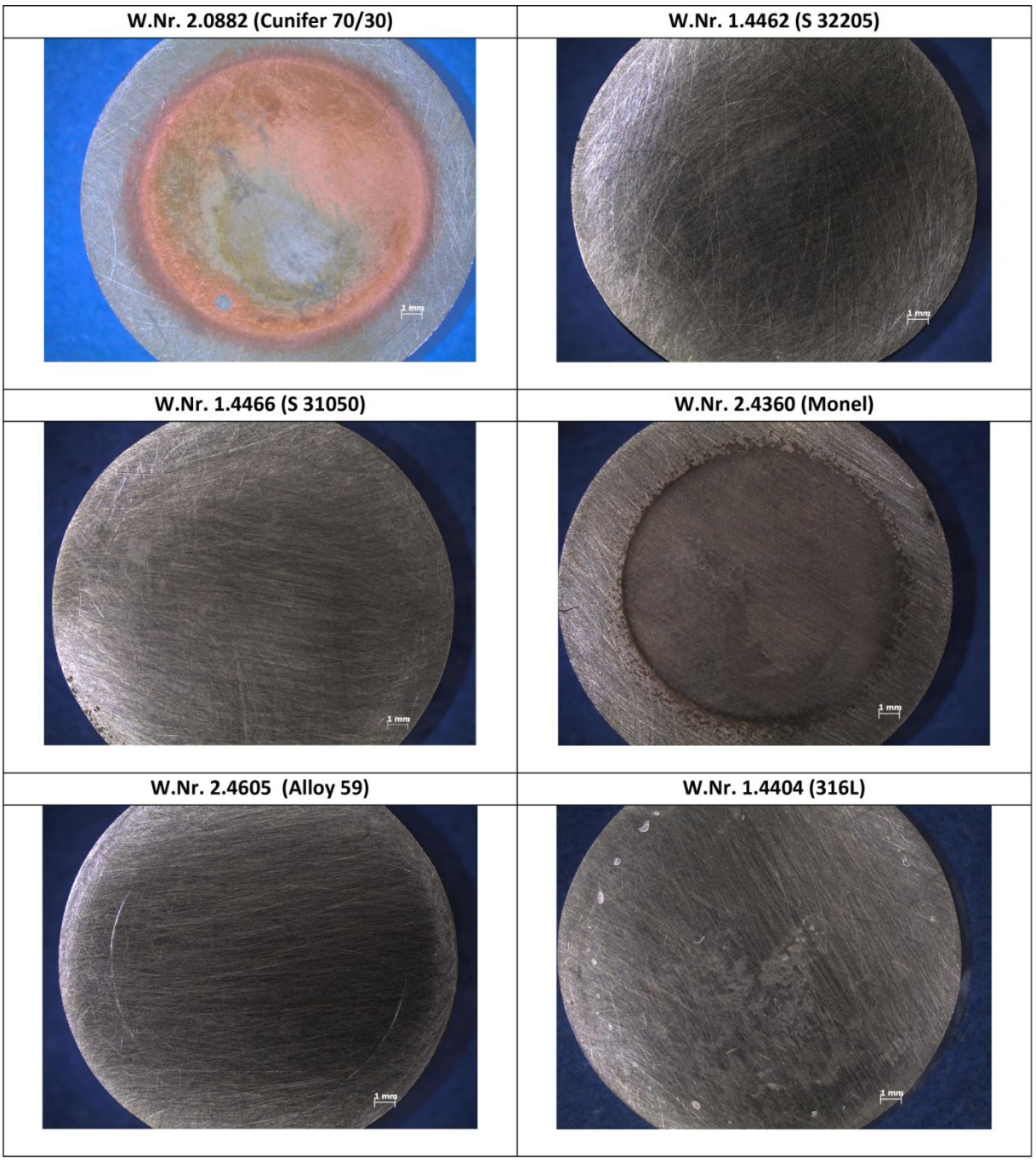


Figure 3. Surface of the samples after the cyclic polarization at (50±2) °C

Sample W.Nr. 1.4462 (S32205), at (50±2) °C has a tendency toward pitting corrosion (Figures 1 and 2). Sample surfaces after cyclic polarization showed no visible signs of pitting corrosion (Figure 3).

Sample W.Nr. 1.4466 (S31050) has similar properties as the sample W.Nr. 1.4462 (S32205) (Tables 2 and 3). Nevertheless, cyclic polarization diagrams (Figures 1 and 2) and sample surfaces after cyclic polarization (Figure 3) show that there is no tendency for pitting corrosion.

Sample W.Nr. 2.4360 (Monel) does not show affinity toward pitting and crevice corrosion, which is evident from the cyclic polarization diagrams (Figures 1 and 2) at both employed temperatures. However, similar to W.Nr. 2.0882, there is a tendency toward selective corrosion (denickelification) particularly at (50±2) °C (Figure 3). This process involves complete dissolution of the alloy followed by redeposition of nobler constituent (copper). It was demonstrated for cupro-nickels and is facilitated in stagnant sea water polluted with ammonia or sulphides [20-22].

Sample W.Nr. 2.4605 (Alloy 59) has low susceptibility toward pitting and crevice corrosion. From cyclic polarization diagrams it is evident that this sample at (50±2) °C behaves as a noble metal. It is obvious that there are no initiated pits on the sample surface (Figure 3).

Sample W.Nr. 1.4404 (316L) has great tendency for pitting corrosion, which is pronounced at (50±2) °C. Figure 3 show initiated pits on the surface of the sample which are significantly more prominent at (50±2) °C.

The results of weight loss measurements in 10 % $FeCl_3$ at (22±2) and at (50±2) °C are presented on Figures 4 and 5. Materials with high content of copper (W.Nr. 2.0882 and W.Nr. 2.4360) showed highest weight loss at both temperatures during 72-hour period, due to the preferential selective corrosion occurrence.

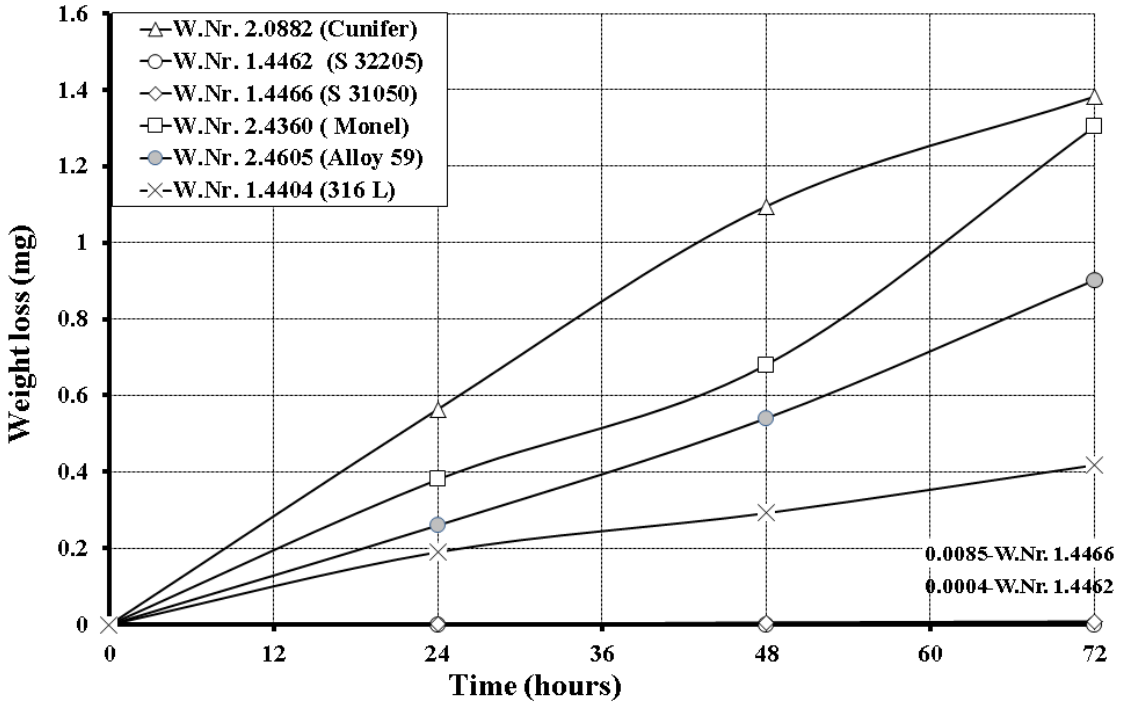


Figure 4. Weight loss measurements in 10 % $FeCl_3$ at (22±2) °C

At elevated temperature the weight loss was approximately double when compared to ambient temperature. Negligible weight loss values at (22±2) °C were recorded on duplex W.Nr. 1.4462 and austenitic stainless steel W.Nr. 1.4466 and are written down at right corner on Figure 4. At elevated temperature those alloys showed substantial and similar weight loss (approx. 1.1-1.2 g). Those values were also similar to alloy W.Nr. 1.4404 at elevated temperature, while at ambient temperature alloy

W.Nr. 1.4404 showed medium weight loss value. Alloy 59, in concordance to DC tests, showed lower weight loss at (50±2) °C then at (22±2) °C. While at (22±2) °C it was substantially high (around 0.9 g), at (50±2) °C it was negligible and the exact value is written down at right corner on Figure 5.

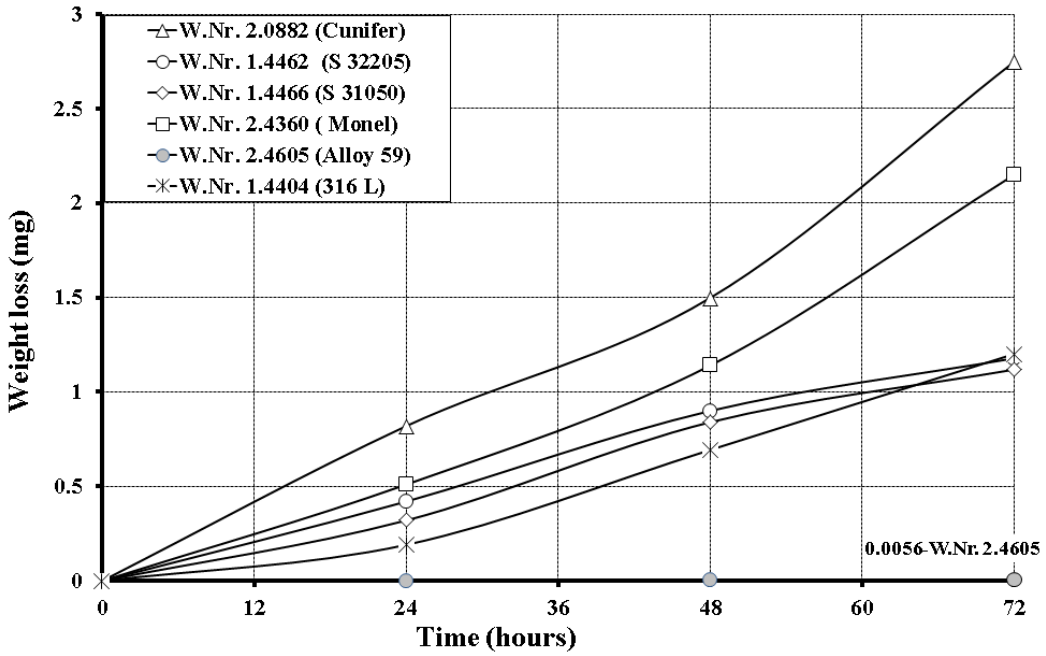
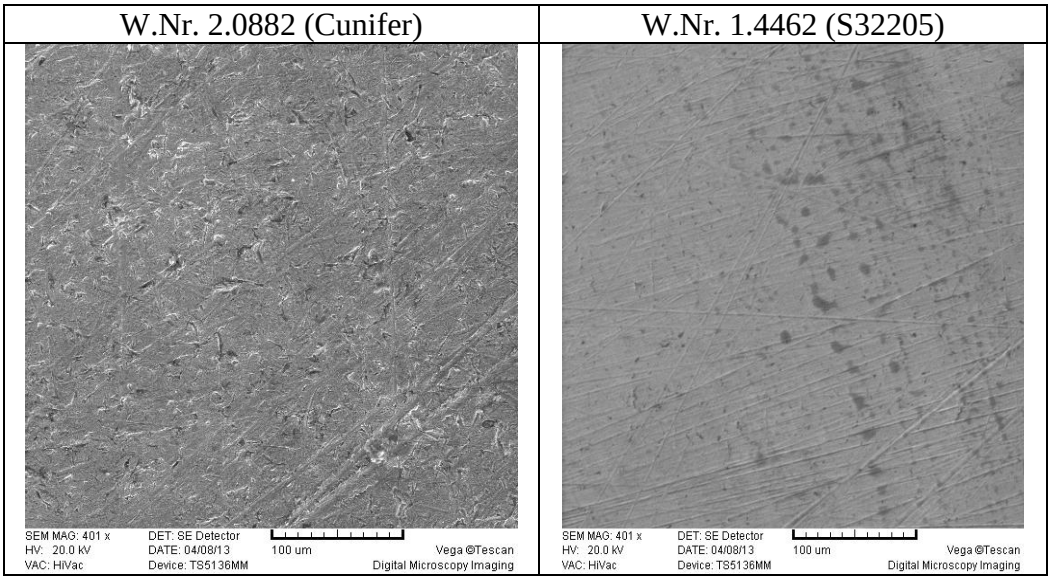


Figure 5. Weight loss measurements in 10 % $FeCl_3$ at (50±2) °C

Scanning electron micrographs of the surfaces of alloy specimens after the weight loss measurement at (50±2) °C are presented on Figure 6. The surfaces of the specimens are in correlation with previously described results. Stainless steels displayed rather clean surface with exception of 316 L which had several distinctive pit initiation sites on the surface. Materials with high content of copper (W.Nr. 2.0882 and W.Nr. 2.4360) showed non homogenous surface resulted from selective corrosion.



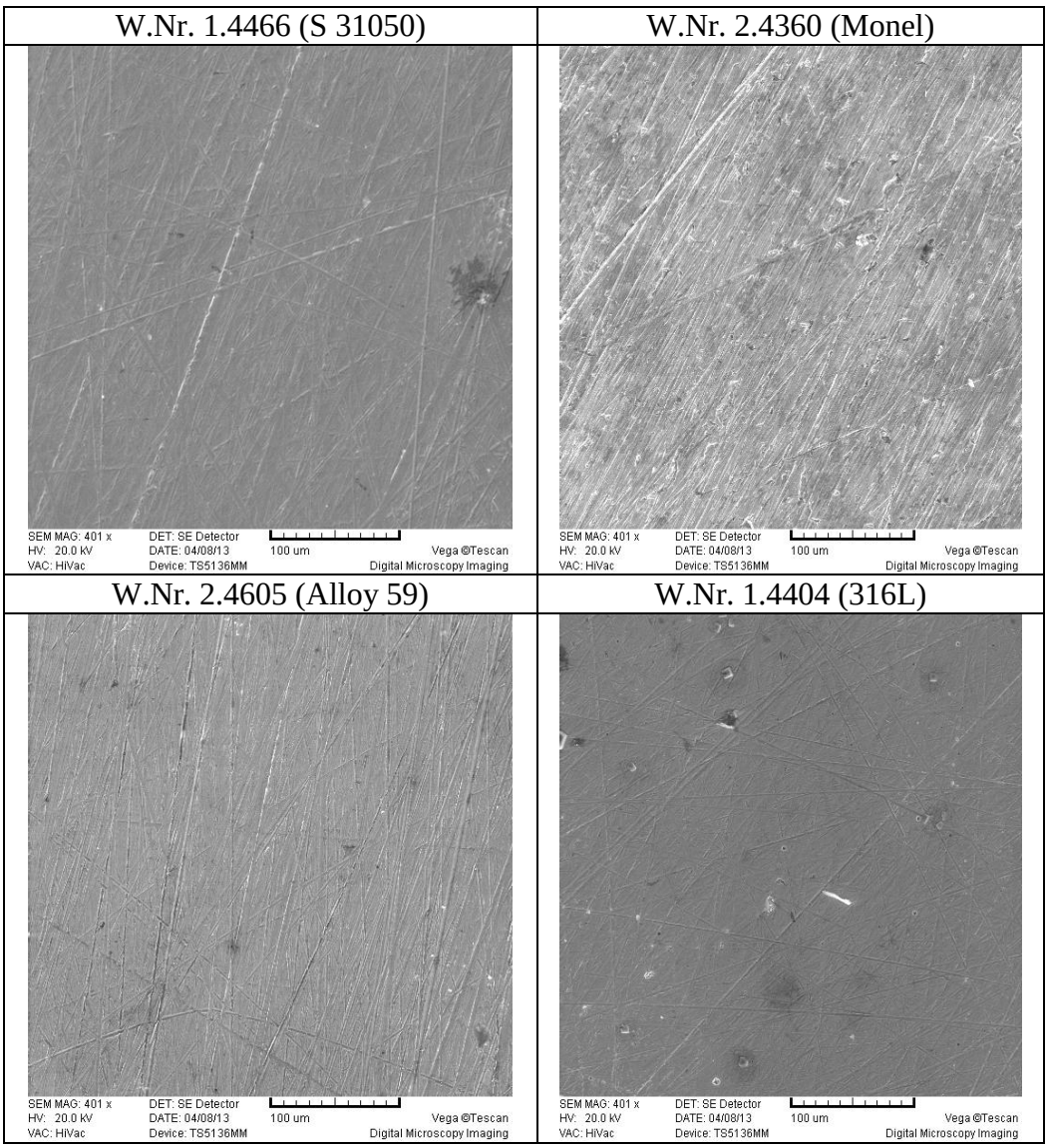


Figure 6. Scanning electron micrograph of the surfaces of tested specimens after weight loss measurements in 10 % $FeCl_3$ at (50±2) ° C

4. DISCUSSION

Test results for all samples (except for sample 5) indicate significantly higher corrosion resistance at (22±2) °C compared to (50±2) °C (Tables 2 and 3).

W.Nr. 2.0882 (Cunifer) does not show tendency for pitting corrosion (Figures 1 and 2) at both employed temperatures. It is well known that copper-nickel alloys are highly resistant to chloride pitting corrosion in broad temperature range, but sulphides can cause pitting, especially when aerated water is mixed with sulphide containing water. Ferrous sulphate dosing is practical solution to this problem [22].

Because of its excellent resistance to seawater corrosion Cunifer is recommended and used in several marine applications i.e. for heat exchange and condenser tubes, piping, platform sheating,

seawater cooling systems, MSF desalination plants and boat hulls [23]. Nevertheless, in this research it was found that cyclic polarisation and immersion in 10% $FeCl_3$ (Figures 3 and 6) give rise to pronounced selective corrosion process. Selective corrosion (denickelification) is infrequent in 70/30 copper-nickels, but low flow rates, deposits, polluted seawater and high temperatures can lead to the occurrence of this phenomenon. The solution is more frequent cleaning, ferrous sulphate dosing or application of suitable CP method [22].

Electrochemical experiments confirmed that the pitting corrosion tendency of the duplex steel W.Nr. 1.4462 (S32205) increases with temperature (Figures 1 and 2), whereas general corrosion rate is similar at both employed temperatures (Tables 2 and 3). Weight loss at room temperature is almost minimal while at elevated temperature is evident (Figures 4 and 5). This indicates that this material, although very convenient at room temperature, is not suitable for use in seawater at elevated temperatures unless cathodic or galvanic protection is applied.

W.Nr. 1.4466 (S31050) sandvik steel shows low resistance to pitting corrosion at both employed temperatures (Figures 1 and 2). It is resistant to general corrosion at both employed temperatures, although the resistance is slightly lower at (50±2) °C (Tables 2 and 3). Similar to W.Nr. 1.4462 weight loss at room temperature is almost minimal, while at elevated temperature is evident (Figures 4 and 5).

W.Nr. 2.4360 (Monel) is mainly resistant to pitting corrosion (Figures 1 and 2). However, when unprotected in quiet seawater Ni-Cu alloys can become susceptible to localised corrosion which is initially rapid but afterward tends to slow down [24]. In sulphide-polluted seawater the resistance to pitting is decreased. Low levels of chlorination can reduce susceptibility to pitting [25]. Protective properties of Monel are similar to Cunifer, although more resistant toward selective corrosion, but still subject to the same. Material loss was obvious already at (22±2) °C, whereas at (50±2) °C it was even more expressed (Figures 3 and 6). In recent papers selective electrodissolution of nickel and copper enrichment on the surface of the Monel alloy immersed in seawater and 3.5 % NaCl solution was determined [26, 27]. Therefore, such material is suitable for conditions in which the main requirement is to avoid pitting and crevice corrosion, otherwise appropriate protection is required (i.e. CP).

Sample W.Nr. 2.4605 (Alloy 59) showed the best protective properties regarding localised corrosion (Figures 1-3 and 6). Moreover, this alloy showed higher corrosion resistance at (50±2) °C compared to (22±2) °C (Tables 2 and 3, Figures 4 and 5). Since alloy 59 is corrosion resistant even under extreme conditions such as high temperatures, chlorination and low pH, this is presumably due to the evaporation of dissolved oxygen from 3.5 % NaCl solution at (50±2) °C.

Considering the literature data [7, 14, 17-19] and the results from this research, it can be concluded that this material is highly suitable for use in particularly aggressive environments where both selective and pitting corrosion are to be avoided.

W.Nr. 1.4404 (316L) is resistant toward general corrosion (Tables 2 and 3), but is extremely susceptible to pitting corrosion at (22±2) °C and at (50±2) °C (Figures 1, 2 and 6). Therefore, without galvanic or cathodic protection, this material is not suitable for use in seawater environments.

Lowest corrosion current density and corrosion rate was determined on sample W.Nr. 2.4605 (Alloy 59), which was the most resistant to pitting and crevice corrosion, at (50±2) °C. Samples W.Nr. 1.4462 (S32205) and W.Nr. 1.4466 (S31050) showed very similar protective properties, and regarding

corrosion rate and preferences toward pitting corrosion they are inferior to the sample W.Nr. 2.4605 (Alloy 59). Sample W.Nr. 2.4360 (Monel) has a minor tendency for pitting corrosion, but it is subject to selective corrosion; by the density of corrosion current, it is inferior to samples W.Nr. 1.4462 and W.Nr. 1.4466. Samples W.Nr. 1.4404 (316L) and W.Nr. 2.0882 (Cunifer) were shown to be the least suitable option in the applied aggressive conditions. 316L is extremely susceptible to pitting corrosion, while Cunifer has the highest density of corrosion current and corrosion rate. The results of Mourao, et al. [14], point to a significantly faster initiation of pits formation in artificial see water (increase of 60 %) at 60 °C, compared to ambient temperature which is in concordance with the results obtained in this paper.

5. CONCLUSIONS

Studied materials showed different corrosion resistance reflecting their different chemical composition (Table 1). Since proper selection of materials is crucial, it is very important to estimate and predict their properties in real working conditions.

Material with the highest percentage of chromium, molybdenum and nickel showed the best corrosion resistance properties. Materials with a high percentage of chromium and iron, and relatively low proportions of molybdenum and nickel, have shown high-quality protection against corrosion at (22±2) °C, while at (50±2) °C this protection was not sufficient. Materials that consist primarily of nickel and copper showed solid properties regarding pitting corrosion, but they were very susceptible to selective corrosion. For these materials possible solution is to apply appropriate galvanic or cathodic protection.

Therefore, according to the presented results the best solution for field use in aggressive conditions (seawater, high temperature) is a material with very high percentages of chromium and molybdenum if main requirement is to avoid selective corrosion and material with high levels of copper if pitting corrosion is to be avoided.

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